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The IR spectrum of OAlF in neon and argon matrices has been recorded. Two of the three expected IR active frequencies were observed. Assuming a linear structure, $O=Al-F$, the argon matrix frequencies were assigned as follows: $\nu_1 = 386\text{cm}^{-1}$ and $\nu_2 = 1022\text{cm}^{-1}$. The unobserved AlF stretching frequency ν_3 was estimated at 675cm^{-1} .

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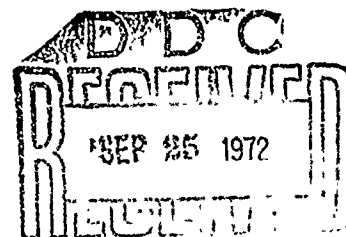
INFRARED MATRIX ISOLATION SPECTRA OF OAlF

By Alan Snelson
IIT Research Institute
Chicago, Illinois 60616

23 August 1972

ABSTRACT

The IR spectrum of OAlF in neon and argon matrices has been recorded. Two of the three expected IR active frequencies were observed. Assuming a linear structure, O=Al-F, the argon matrix frequencies were assigned as follows:
 $\nu_2=386\text{cm}^{-1}$ and $\nu_3=1022\text{cm}^{-1}$. The unobserved AlF stretching frequency ν_1 , was estimated at 675cm^{-1} .



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INTRODUCTION

The reaction between AlF_3 and Al_2O_3 at temperatures just below the melting point of Al_2O_3 has been studied in an effusion experiment⁽¹⁾. Based on thermodynamic evidence, and by analogy with the formation of OBF in the $\text{BF}_3 + \text{B}_2\text{O}_3$ system at elevated temperatures, the major vaporizing aluminum-fluorine oxygen species was assumed to be OAlF. No other studies have been reported confirming the existence of OAlF. An investigation of the $\text{AlF}_3 + \text{Al}_2\text{O}_3$ system at high temperatures using the matrix isolation technique was therefore undertaken in an effort to obtain spectral evidence for OAlF.

EXPERIMENTAL

The matrix isolation equipment used in this study has been described previously⁽²⁾. Liquid helium was used as the refrigerant and Matheson research grade neon and argon for the matrix gases. Baker reagent grade aluminum fluoride and Alsimag alumina, 99.8% Al_2O_3 were used in all experiments. The alumina was in the form of a tube, 1/4" O.D. x 1/8" I.D. x 5" long, with an effusion orifice of 0.025". Aluminum fluoride powder in the end of the tube remote from the effusion orifice, was heated by a resistance furnace at 850-900°C. The AlF_3 vapor reacted at the high temperature orifice end of the alumina tube, and was maintained at 2225-2275°C over

a length of about 3 cm, by radiation heating from a tantalum susceptor, inductively heated. To minimize possible reaction between the effusing vapors and the tantalum susceptor, a sleeve of rhenium foil was interposed between the tantalum and the alumina tube. The effusing vapors were isolated over periods up to six hours in neon or argon matrices in a total of twenty-two experiments. Spectral measurements were made on a Perkin Elmer 621 spectrophotometer over the range 4000-200 cm^{-1} . Reported frequencies are believed to be accurate to $\pm 1 \text{ cm}^{-1}$.

RESULTS

In all experiments the most intense absorption bands were always those of $\text{AlF}_3^{(2,3)}$, however other absorption bands, some with moderate intensity, also appeared. Previous experience with the matrix isolated vapor species over AlF_3^3 , $\text{AlF}_3 + \text{Al}^3$, Al_2O_3^4 and $\text{Al}_2\text{O}_3 + \text{Al}^5$ proved conclusively that the "other" absorption bands appearing in the $\text{Al}_2\text{O}_3 + \text{AlF}_3$ system could not be assigned to either AlF_x or AlO_x species. It appears reasonable to assign these bands to some species containing all three elements. Under the best conditions of isolation, nine absorption bands, assignable to AlO_xF_y species were recorded. The strongest of these in an argon matrix are shown in Figure 1 (dotted curves). The form of the spectrum obtained in a neon matrix was identical to that

in an argon matrix, and for this reason is not shown. Unfortunately under good conditions of isolation it was not possible to obtain most of these bands even with moderate absorption intensity due to the very poor transparency of the matrix. This was attributed to the scattering caused by the relatively large amount of the inert gas required for effective isolation of the species due to the high temperature at which the furnace was operated. Further, the actual matrix dilution factors could not be calculated since the amounts of the AlO_xF_y species vaporizing was not known. The efficiency of the isolation was judged therefore by the appearance of the AlF_3 spectra for which much data have been acquired in this laboratory^(2,3) under different conditions of isolation. Matrix isolation conditions are quoted simply as either good or poor on this basis. Under poor conditions of isolation many of the absorption bands appearing previously with low intensity under good conditions of isolation could be made to appear with moderate intensity and some new features also occurred. Parts of a typical spectrum obtained under poor conditions of isolation are shown in Figure 1 (solid line).

Relative absorption band intensity measurements made on the two strongest bands shown at A and F in Figure 1 appearing in the spectrum under good isolation conditions, were constant to within 4.5%, suggesting that these two features may be

assigned to the same molecular species. Relative absorption band intensity measurements made on other features in the spectrum with respect to the band at A and F did not indicate that any of these absorptions could be assigned to the same molecular species as those at A and F. In a few cases the absorption band intensities were so low and obvious overlapping of different absorption bands occurred, that meaningful relative intensity measurements could not be made. An example of this behavior is shown at D in Figure 1. Under poor conditions of isolation two relatively new strong features appear at E and C, in addition to the one at D which is the only feature occurring in this region under good isolation conditions. The presence of the bands at E and C effectively prevented good intensity measurements being made on the band at D. However it is quite obvious in this case that the band at D can in no way be associated with the same molecular species that is responsible for the bands at E and C. Thus, although quantitative absorption band relative intensity measurements could not be made on all features in the spectrum, it was possible, from the overall form of the spectra under good and poor isolation conditions, to determine that none of the weaker features could possibly be associated with the two strongest absorption bands at A and F with one possible exception. This was the absorption feature at D.

ABSORPTION BAND ASSIGNMENT

Based on the experimental observations it is reasonable to conclude the two absorption bands shown at A and F in Figure 1 may be assigned to the same molecular species, and that this species is the major AlO_xF_y vapor phase constituent formed in the $\text{AlF}_3 + \text{Al}_2\text{O}_3$ reaction. The fact that only two absorption bands may definitely be assigned to this species in the $200\text{-}4000\text{ cm}^{-1}$ region suggests that the molecule responsible contains a small number of atoms. Even if the absorption band at D were definitely related to those at A and F, a triatomic molecule could still account for all three absorption features. The possibility that some absorption bands may lie below 200 cm^{-1} which are definitely related to those at A and F cannot be excluded since this region was not accessible to spectroscopic observation in this study.

The possibility that the two absorption bands at A and F may be assigned to a molecular species OAlF will be examined. If indeed a species OAlF exists, three ir-active frequencies may be expected independent of the particular molecular geometry or ordering of the atoms. The ordering of the atoms OAlF rather than AlOF would be expected on energetic grounds. The former configuration is also suggested by comparison with the analogous linear boron molecules $\text{OBX}^{(6,7)}$ ($\text{X}=\text{F}, \text{Cl}$ or Br) which might be expected to have similar bonding

characteristics. In the latter species it was shown that the oxygen-boron and the boron-halide stretching frequencies were of the same order of magnitude as the stretching frequencies in the respective diatomic, B=O and tetratomic, BX_3 molecules. If a linear geometry for the OAlF species is assumed and the stretching force constants in Al=O⁽⁸⁾ and AlF₃⁽²⁾ used to calculate the postulated OAlF stretching frequencies, values of approximately 1050 and 650 cm^{-1} are obtained. The higher frequency, corresponding presumably to the Al=O vibration mode, is close to the observed frequency of the band at A, shown in Figure 1 at 1022 cm^{-1} . That no absorption band was observed at about 650 cm^{-1} which could definitely be assigned to the same molecular species as that at A and which would be expected on the basis of the assumed force constants is disappointing. This does not negate entirely the proposed molecular structure and calculated vibration frequencies, since it is possible that the Al-F stretching mode has a low extinction coefficient. Indeed such a situation exists for the B-X stretching modes in the comparable OBX molecules^(6,7). Assuming the non-appearance of the Al-F stretching frequency is due to a low extinction coefficient in the present investigation, the lower frequency shown at F in Figure 1 at 386 cm^{-1} may be assigned to the OAlF bending mode.

In Table I the results of a force constant calculation based on the assumed frequency assignment and linear geometry

TABLE I

VIBRATION FREQUENCIES (cm^{-1}) AND FORCE CONSTANTS OF AlF_3 ASSUMING $C_{\infty v}$ SYMMETRY

Vibrational Mode	Neon Matrix	Argon Matrix	Calculated(a)
ν_1			675
ν_2	389	386	386
ν_3	1027	1022	1022

$$k(\text{Al=O}) = 4.46 \times 10^5 \text{ dynes cm}^{-1} \quad k(\text{Al-F}) = 4.9 \times 10^5 \text{ dynes cm}^{-1}$$

$$k_{\delta/1_1 1_2} = 0.33 \times 10^5 \text{ dynes cm}^{-1}.$$

(a) Force constant calculation based on the observed argon matrix frequencies and on assumed value of $k(\text{Al-F}) = 4.9 \times 10^5 \text{ dynes}$.

is given. For the purpose of this calculation $k(\text{Al-F})$ was estimated at $4.9 \times 10^5 \text{ dyne cm}^{-1}$, the same as in $\text{AlF}_3^{(3)}$. The resulting value of $k(\text{Al=O})$ in OAlF at $4.46 \times 10^5 \text{ dyne cm}^{-1}$ is somewhat lower than the value of $k(\text{Al=O}) = 5.51 \times 10^5 \text{ dyne cm}^{-1}$ in diatomic AlO . A similar trend is found for the boron-oxygen force constants in OBX and BO species. In calculating the OAlF bending force constant, it was necessary to estimate values for the bond lengths $r(\text{Al=O}) = 1.62\text{\AA}$ and $r(\text{Al-F}) = 1.65\text{\AA}$. These values are the same as in the diatomics $\text{AlO}^{(8)}$ and $\text{AlF}^{(9)}$, respectively, and an OAlF bending force constant of $k_{\delta/1_1 1_2} = 0.33 \times 10^5 \text{ dyne cm}^{-1}$ was obtained. This value is larger than the AlF_3 in-plane-bending force constant of $0.19 \times 10^5 \text{ dyne cm}^{-1}$. The bending force constants in the OBX species were found to be larger than the in-plane values in BX_3 and smaller than the in-plane values found for the OBO group in B_2O_3 and LiBO_2 . At the present time there are no data available as to the value of bending constants in the OAlO group thus a comparison between the bending force constants of OBF and OAlF is not possible.

It was noted earlier that a weak absorption feature appearing at D in Figure 1 at 687 cm^{-1} could possibly be related to the two stronger features at A and F though this could not be proved by absorption band relative intensity measurements for reasons given. The calculated value for this frequency at 675 cm^{-1} is close to that of the observed band

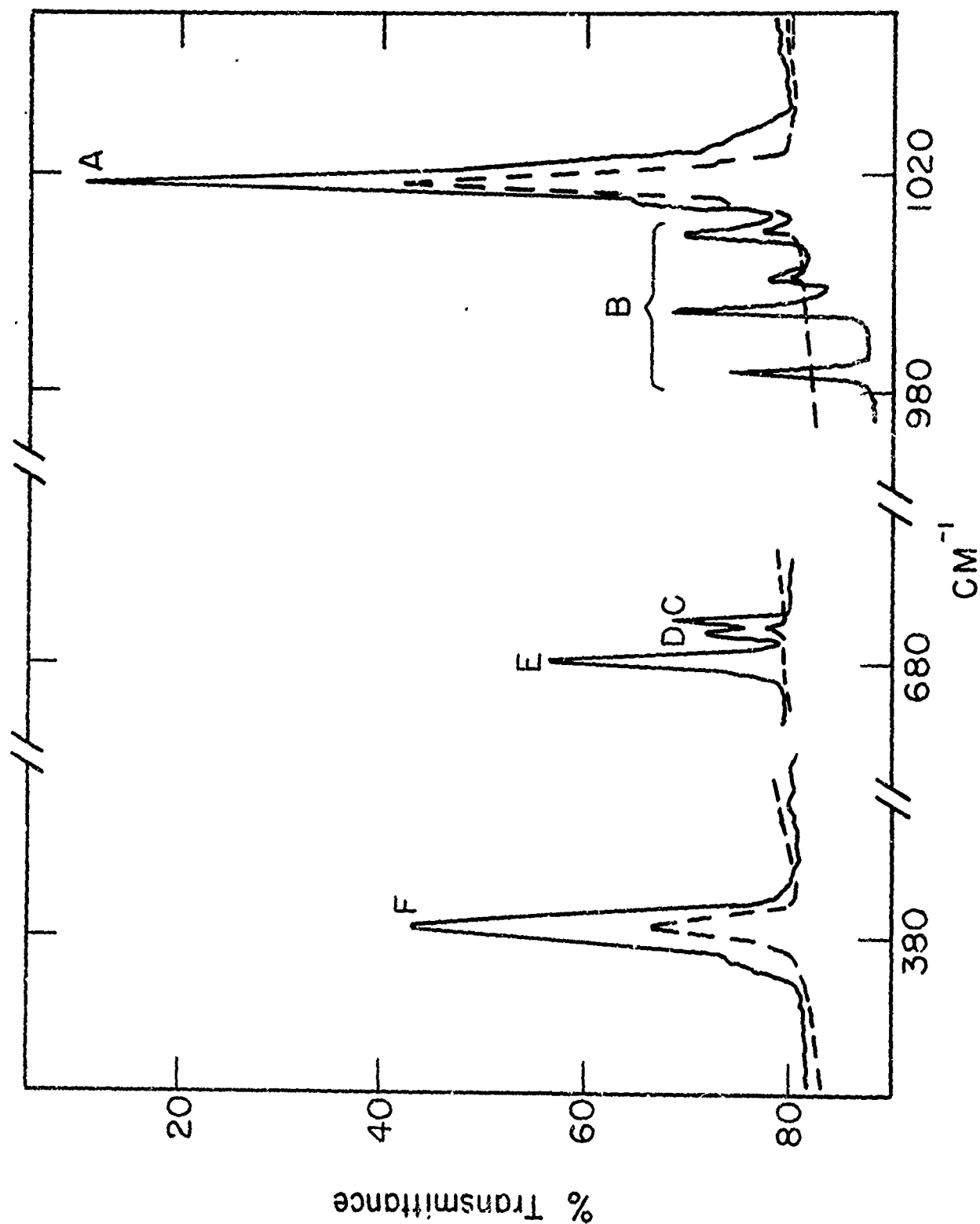


Figure 1

INFRARED SPECTRUM IN AN ARGON MATRIX OF THE VAPOR SPECIES FORMED IN THE REACTION $\text{Al}_2\text{O}_3(\text{s}) + \text{AlF}_3(\text{g})$ AT HIGH TEMPERATURE. DOTTED CURVE, GOOD ISOLATION CONDITIONS, DEPOSITION TIME, 2 HRS. SOLID CURVE, POOR ISOLATION CONDITIONS, DEPOSITION TIME 2.5 HRS.

at D and suggests that this band may indeed correspond to the Al-F stretching mode in OAlF.

CONCLUSION

The spectral data obtained in this study clearly indicates that the reaction of AlF_3 at high temperature with Al_2O_3 produces at least one volatile species containing, aluminum, oxygen and fluorine. Since isotopic studies were not made, a definitive identification of the species cannot be made on the basis of the observed spectra. An assignment of the two observed major absorption bands to a linear molecule OAlF appears reasonable based on a comparison of the derived force constants with those obtained for the analogous OBX species.

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